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Photoelectrochemical Measurement of Phthalic Acid Adsorption on Porous TiO₂ Film Electrodes

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ABSTRACT

A new adsorption measurement method based on photoelectrochemical oxidation principle has been developed. The method can be used to directly quantify the amount of adsorbates at TiO_2 electrode surface in a sensitive and accurate manner. The adsorption of phthalic acid on TiO_2 was studied as a test case. The relationship between the amount of the adsorbate at TiO_2 surface and the concentration of phthalic acid in the solution was obtained. The adsorption of phthalic acid on TiO_2 surface was proved to follow Langmuir adsorption model. For the first time, the adsorption equilibrium constant of an adsorbate at TiO_2 surface has been photoelectrochemically measured. The adsorption equilibrium constant of phthalate on TiO_2 porous film at pH 4.0, $K=4.0 \times 10^4 \text{ M}^{-1}$, was obtained using our method, which was close to that obtained by conventional methods. The effect of solution pH on the amount of adsorbate at TiO_2 surface was also investigated. The results indicate the adsorption of phthalic acid is mainly of chemical bond nature.

Key words: Nanoporous TiO_2 film; Adsorption; photoelectrochemistry; phthalic acid

1. INTRODUCTION

In recent years, photocatalytic processes at the semiconductor TiO_2 have been used to great effect in the oxidative degradation of organic compounds in solution[1-7]. The theoretical basis of TiO_2 photocatalysis has been well established and known to involve light induced photogeneration of electron-hole pairs within the semiconductor catalyst.[3, 6, 8] These electron-hole pairs dissociate into free photoelectrons in the conduction band (e_{cb}^-) and photoholes in the valence band (h_{vb}^+). The photohole formed on TiO_2 is a very powerful oxidising agent ($E^0 = +3.1\text{V}$ vs NHE) that will readily lead to the oxidation of a species adsorbed at the TiO_2 /liquid interface. In this way, direct oxidation of adsorbed organic material and/or solvent molecules can take place.

Although a great deal of progress has been made, significant effort to improve the overall efficiency of TiO_2 photocatalytic oxidation process is still being investigated. To this end a wealth of fundamental adsorption and kinetic studies have been carried out to gain a better understanding of the photocatalytic processes with a view to improving photocatalytic efficiencies [9-14].

Most of the reported kinetic studies of TiO_2 photocatalytic oxidation of organic compounds have been described by Langmuir-Hinshelwood kinetic models [3, 6, 9, 13, 15]. All of these models employ the surface concentration/coverage of reactants to describe the reaction rate. However, problems associated with accurately identifying and employing such models is often relied on the accurate measurement of the surface concentration/coverage of reactants.

Typically, adsorption at TiO_2 surfaces are conducted by employing large surface area TiO_2 nanoparticle slurries [2, 11, 16-18]. This is done to ensure that measurable amounts of adsorbate

will be removed from solution. The amount of adsorbed species is usually calculated by measuring the decrease in concentration of adsorbate in solution after separation of the slurry. Apart from the practical problems associated with this approach, there are many uncontrollable factors involved in such a measurement that result in a great difficulty in maintaining desired experimental conditions. The most significant of these are facts that adsorbate concentration in the bulk solution can change appreciably and rapidly during adsorption and the pH can also change for some adsorbates due to the deprotonation/protonation during adsorption. As a consequence, maintaining certain experimental conditions is very difficult and the adsorption value would be different from that under specified conditions.

In this study, we propose an *ex-situ* photoelectrochemical method to accurately quantify the adsorption of organic compounds on the TiO_2 surface. The method involves two steps. A TiO_2 porous film electrode is immersed in the sample solution containing adsorbates for a given time to allow adsorption and the electrode is then removed from the sample solution into the detection solution containing the supporting electrolyte only to perform the photoelectrochemical measurement. The current generated from photoelectrochemical oxidation of the adsorbate was used to quantify the extent of surface coverage. Immobilisation of TiO_2 onto a conducting substrate makes the application of photoelectrochemical techniques possible. The adsorbate concentration depletion and pH changes in the bulk solution caused by the adsorption are reduced to negligible proportions due to a large solution volume to electrode area ratio. The high sensitivity of electrochemical techniques ensures accurate measurement even at very low surface coverage. Phthalic acid was used as the adsorbate to test the method due to its known strong adsorption onto TiO_2 surfaces [19]. The adsorption isotherm of phthalic acid was obtained and

the binding constant was determined according to Langmuir adsorption model. The effect of pH on phthalic acid adsorption was also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials: Indium Tin Oxide (ITO) conducting glass slides ($8\Omega/\text{square}$) were commercially supplied by Delta Technologies Limited. Titanium butoxide (97%, Aldrich) and potassium hydrogen phthalate (AR, Aldrich) were used as received. All other chemicals were of analytical grade and purchased from Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., $18\text{M}\Omega\text{ cm}$).

2.2. Preparation of the porous TiO_2 film electrode:

Aqueous TiO_2 colloid was prepared by hydrolysis of titanium butoxide according to the method described by Nazeeruddin et.al[20]. The resultant colloidal solution contains 60g dm^{-3} of anatase TiO_2 nanocrystals with particle size ranging from 8 to 10nm. The ITO slide was used as the electrode substrate and was pretreated by washing in turn with detergent, water, chromic acid washing solution and ethanol. After pretreatment, the ITO slide was dip-coated in the TiO_2 colloidal solution. The coated electrodes were then calcined in a muffle furnace at 450°C for 30 minutes in air. The thickness of the anatase TiO_2 nanoporous film was $1\mu\text{m}$ measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

2.3. Apparatus and methods.

All photoelectrochemical experiments were performed at 23°C in a three-electrode electrochemical cell with a quartz window for illumination. The TiO_2 film electrode was employed as the working electrode and placed in an electrode holder with ca. 0.65cm^2 left

unsealed to be exposed to the solution for illumination and photoelectrochemical reaction. A saturated Ag/AgCl electrode and platinum mesh were used as the reference and the auxiliary electrodes respectively. A voltammograph (CV-27, BAS) was used for application of potential bias in the photoelectrolysis experiments and linear potential sweep experiments. Potential and current signals were recorded using a Macintosh computer (7220/200) coupled to a MacLab 400 interface (AD Instruments). Illumination was carried out using a 150W xenon arc lamp light source with focusing lenses (HF-200w-95, Beijing Optical Instruments). To avoid the sample solution being heated-up by the infrared light, the light beam was passed through an UV-band pass filter (UG 5, Avotronics Pty. Limited) prior to illuminating the electrode surface.

The linear potential sweep experiments were carried out at the indicated scan rates with a light beam of constant intensity continuously illuminating the porous TiO₂ working electrode. With the photocurrent transient experiments, a constant potential bias of +0.20V was applied to the electrode and the illumination was switched on and off with a manual shutter.

The measurement of phthalate adsorption was conducted in two steps. The pre-adsorption of phthalic acid was performed by immersing the TiO₂ coated electrode in sample solutions containing 0.1M NaNO₃ and various concentrations of potassium hydrogen phthalate for 30 minutes. After the pre-adsorption, the electrode was removed from the sample solution and immediately washed with 0.1M NaNO₃ before it was transferred into a blank solution (0.1M NaNO₃), where the illumination of electrode was switched on and the adsorbed phthalate molecules were degraded. The photocurrent response resulted from the degradation of pre-adsorbed phthalate molecules were recorded under +0.20V applied potential bias and the illumination of 6.6mW/cm² light intensity. The total charge was obtained by integrating the photocurrent during the degradation period with the background charge deducted.

All experiments were carried out using unbuffered electrolyte (0.1 M NaNO_3). The pH of the solution was adjusted with nitric acid or sodium hydroxide solution and was closely monitored during experiment with a pH meter

3. RESULTS AND DISCUSSION

3.1. Applied Potential Bias for Photoelectrolysis

The effect of applied potential bias on the photoelectrochemical oxidation of phthalic acid was first investigated. The photocurrent-potential characteristics of the electrodes were obtained in the presence and absence of phthalate by linear sweep voltammetry at a rate of 10 mV/s between -0.30 to 0.50V vs Ag/AgCl (Figure 1). The result shows that the photocurrent increases linearly with the potential bias in the low potential region and then reaches saturation. This is similar to the photocurrent-potential relationship obtained from a porous TiO_2 electrode in a methanol solution as discussed in our previous publication[21]. Such photocurrent-potential relationship may be explained as follows. For a given light intensity, the concentration of photogenerated electron-hole pairs or the rate of electron-hole pair generation is constant. The actual rate of electrons reaching the back contact and the current, depends on two factors, the electron transport in the film and photohole capture process at the TiO_2 /solution interface, which are vital to the suppression of electron-hole pair recombination. Before the photocurrent reaches saturation with respect to potential, the electron transport across the film is the rate-determining step, as a result a linear relationship is obtained related to the film resistance. Increasing the electron transport rate by increasing the applied electric field, the rate of reduction of the photogenerated hole becomes the dominant factor resulting in photocurrent saturation. In this study, a $+0.20\text{V}$ potential bias was selected for all subsequent experiments. This was chosen such

that the potential bias was sufficient to suppress the recombination of photoinduced electron hole pairs but not so positive as to lead to direct electrochemical oxidation of water at the the ITO substrate, which complicates the adsorption measurements.

3.2. In-situ Transient Photocurrent Response

During linear sweep voltammetry experiments in phthalic acid 0.1M nitrate solution a photocurrent spike was observed as the illumination was turned on. This phenomenon has never been reported for photoelectrochemical oxidation of oxalate at TiO_2 porous film electrodes. The authors believe this behaviour is related to the consumption of adsorbed oxalate rather than double layer charging and discharging process [22, 23]. To clarify what cause this phenomenon in-situ light-on and light-off experiments were run in phthalic acid solution. Figure 2 shows the transient photocurrent responses obtained under +0.20V applied potential with different light-off time duration from a 0.10 M NaNO_3 solution (pH 4.0) containing 10 μM potassium hydrogen phthalate. A sharp photocurrent spike was observed immediately after the light was switched on which then decayed back to a steady photocurrent. The result also revealed that the magnitude of the photocurrent spike and spike area increased as the time of the dark period increased. The steady-state photocurrent was independent of the time of dark period. The transient response of photoelectrodes has long been observed and studied. Though the transient response often reflects the charging or discharging of space charge layer and electric double layer capacitance [24], nevertheless, the transient photocurrent observed here is unlikely due to the charging or discharging of capacitance. It is likely due to faradic photoelectrochemical process caused by degradation of adsorbed phthalate. This is evident from the fact that the time domain of the transient observed was much longer than the normal capacitance response of space charge layer and electric double layer. Further more, the spike area was found to be dependent on the non-

illumination time length and on the phthalate concentration, which is, in turn, related to the surface coverage of phthalate. This prompted us to quantitatively measure adsorption by this photoelectrochemical method.

3.3. Measurement of Phthalate Adsorption

3.3.1. Quantitative relationship

To avoid the interference of the photoelectrochemical degradation of phthalic acid from bulk solution on the adsorption measurement, an *ex-situ* photoelectrochemical measurement method was proposed. The TiO₂ coated electrode was firstly immersed in the sample solutions containing different concentration of phthalic acid to complete the preadsorption and then transferred to a blank electrolyte solution, where photoelectrolysis was performed. Figure 3 shows the typical photocurrent - time profiles obtained from the electrodes that preadsorbed in phthalic acid and in blank electrolyte solutions. It can be seen that the photocurrent decayed with time and then reached a steady value, which was due to the oxidation of water. It is noted that the blank photocurrent obtained from the electrode preadsorbed in blank electrolyte solution was purely due to the oxidation of water, while the photocurrent obtained from the electrode preadsorbed in phthalic acid solution consists of two current components, one is due to photoelectrochemical oxidation of adsorbed phthalic acid, and the other is due to the oxidation of water, which is the same as the blank photocurrent. Our experimental results showed that the blank photocurrent was essentially constant for the given set of experimental conditions. For a given time period, the charge passed for both cases can be obtained by integration of the photocurrent and blank photocurrent. The charge difference between the two cases is the net

charge due to the photoelectrochemical oxidation of the adsorbed phthalic acid, which is indicated as the shaded area in Figure 3.

Figure 4 shows the relationship between the net charge and the *ex-situ* preadsorption time at a given phthalic acid concentration. It was found that the adsorption equilibrium was reached in less than 10 minutes at relatively high concentration of phthalic acid (40 μ M). At low adsorbate concentration (2.5 μ M), the net charge linearly increases with preadsorption time and then levels off, indicating the adsorption equilibrium. Under such adsorption conditions, the linear relationship between the net charge and adsorption time implies the relationship between net charge and adsorption amount is also linear. This is because the adsorption process is controlled by diffusion under low adsorbate concentration and low surface coverage, and according to Fick's law the adsorption amount should be proportional to the adsorption time. In fact, the linear relationship between the net charge and amount of adsorption obtained here is a direct reflection of Faraday law.

3.3.2. Adsorption Thermodynamics

In order to measure the adsorption isotherm, the time required to reach the adsorption equilibrium under various phthalic acid concentrations were investigated. The results demonstrated that the adsorption equilibrium can be reached within 30 min of *ex-situ* preadsorption for all concentration investigated. After preadsorption in a phthalic acid sample solution for 30 min, TiO₂ porous film electrode was transferred to a 0.1M NaNO₃ blank solution to perform photoelectrochemical measurement. The net charges, Q , were measured by integrating the net photocurrent within the degradation period. As demonstrated in Figure 4, the net charge, Q , is directly proportional to the amount of adsorbed phthalic acid. Figure 5 shows

the relationship between the net charge (amount of adsorbates) and the concentration of phthalic acid in the sample solution (adsorption isotherm). The Langmuir adsorption model has been commonly employed to study the adsorption behaviour of organic compounds on metal oxide surfaces[11, 25].

Assuming a monolayer adsorption structure, we can present the surface coverage, θ , as:

$$\theta = \frac{Q}{Q_{\max}} \quad (1)$$

Where Q is the net charge due to the photoelectrochemical oxidation of adsorbates and Q_{\max} is the maximum net charge at 100% surface coverage.

Langmuir isotherm equation can then be written as:

$$\frac{C}{Q} = \frac{1}{Q_{\max}} C + \frac{1}{Q_{\max}} \frac{1}{K} \quad (2)$$

Where C is the concentration of adsorbate in the sample solution and K is the adsorption equilibrium constant.

Treating the data obtained in Figure 5 according to Langmuir model by plotting C/Q against C gives a straight line with $R^2 = 0.998$ (Figure 6). This implies the adsorption data agrees well with Langmuir adsorption model. The maximum charge, $Q_{\max} = 4.19$ mC, was obtained from the slope of the curve. According to Equation 1, the surface coverage θ can be calculated after the Q_{\max} is determined. The adsorption equilibrium constant, $K = 4.0 \times 10^4 \text{ M}^{-1}$ was obtained from the ratio of the slope to the intercept of the curve (see Equation 2). The K value obtained by this photoelectrochemical method was close to that of phthalic acid adsorption at TiO_2 (Degussa p25)

obtained by Moser and co-workers of $5 \times 10^4 \text{ M}^{-1}$ [19] at pH 3.6. The agreement of adsorption with the Langmuir adsorption model suggests that the molecules form a monolayer coverage.

3.4. Influence of pH on Phthalic acid equilibrium adsorption amount

It is widely accepted that carboxylic group can coordinate with TiO_2 surface to form surface complex [17, 19, 26, 27]. This process can be affected by the solution pH since the speciations of both TiO_2 surface and phthalate molecules are pH dependent due to protonation/deprotonation. Figure 7 shows the functional group speciation change of TiO_2 surface with pH cited from Kormann et. al. [28], the species distribution of phthalic acid with pH and the dependence of the adsorption amount of phthalic acid on pH in sample solution. At pH 4.0 the adsorption reached maximum, which coincides with the maximum fraction of HTh^- . This implies that HTh^- can be favorably adsorbed to TiO_2 surface. Considering the TiO_2 surface carrying positive charge in acidic conditions and HTh^- carrying negative charge, the adsorption can be benefited from the electrostatic attractive force between them. From pH 4.0 to pH 2.0 the fraction of HTh^- species in solution dropped significantly, nevertheless, only a slight decrease in the amount of adsorption was observed. Considering phthalic acid at pH 2.0 mainly exists in neutral molecule form, electrostatic attraction force between molecular form of phthalic acid and electrode surface is insignificant. Therefore, the adsorption is more likely of chemical bonding nature. The sharp decrease in adsorption quantity from pH 4.0 to pH 6.0 indicates the HTh^- was more favorably adsorbed on $-\text{TiOH}$ than Th^{2-} on $-\text{TiOH}$ sites. The adsorption amount remains relatively constant from pH 6.0 to 8.0. It can be seen from Figure 7(a) that the TiO_2 surface is essentially neutral, the electrostatic attraction or repulsion between adsorbate and TiO_2 surface is insignificant. The significant amount of adsorption within this pH range again demonstrates that the adsorption was specific and Th^{2-} can be chemically bound to TiO_2 surface. As pH increased

from 8.0 to 10.0, the negative charge density of TiO_2 surface was increased. As a consequence, the electrostatic repulsion between Th^{2-} and negatively charged TiO_2 surface was increased. This is obviously detrimental to the adsorption, which resulted in a sharp decrease in adsorption amount.

CONCLUSION

In this work, we have established a new adsorption measurement method based on photoelectrochemical oxidation principle. The study of phthalate adsorption has demonstrated the usefulness of the developed method in investigating the adsorption behaviour of adsorbates at semiconductor surface. Quantity of adsorbates, surface coverage and adsorption constant can be determined in a simple, rapid, sensitive and accurate manner. To our knowledge, this is the first time such a measurement principle has been used for this type of applications. The adsorption variation of phthalic acid with pH was investigated and well explained by the speciation changes of the TiO_2 surface and phthalic acid with pH. It was found that the adsorption of phthalic acid onto TiO_2 surface at different pH can be attributed to two different interactions, one is specific adsorption that involves chemical binding and the other is electrostatic interaction between TiO_2 surface phthalic acid of different forms.

The proposed photoelectrolysis method has been demonstrated to be a useful tool for adsorption studies of organic compounds. The photocurrent decay of the adsorbed organic compound also provides a lot of information about the photocatalytic oxidation kinetics of the adsorbed organic compounds at TiO_2 porous film. Investigation into this area is in progress.

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Figure Captions

Figure 1. Voltammograms of the porous TiO_2 electrode in 0.1 M NaNO_3 solution of different potassium hydrogen phthalate concentrations at pH 4.0, at 6.6 mW/cm^2 light intensity and at scan rate 10 mV/s : (a) no potassium hydrogen phthalate; (b) $10 \text{ }\mu\text{M}$; (c) $30 \text{ }\mu\text{M}$; (d) $50 \text{ }\mu\text{M}$; (e) $75 \text{ }\mu\text{M}$; (f) $125 \text{ }\mu\text{M}$.

Figure 2. The in-situ transient photocurrent/time profile for different pre-adsorption time, from a solution of $10 \text{ }\mu\text{M}$ potassium hydrogen phthalate, measured in 0.1 M NaNO_3 solution at pH 4.0 .

Figure 3. The ex-situ transient photocurrent/time profile of a anatase TiO_2 nanoporous electrode in 0.1 M NaNO_3 after it was ex-situ preadsorbed in $5 \text{ }\mu\text{M}$ phthalic acid + 0.1 M NaNO_3 solution at pH 4.0 for 8 minutes(dash line) and an electrode with no pre-absorbed phthalic acid (Solid line).

Figure 4. The charge dependence on ex-situ preadsorption time after preadsorbed in 0.1 M NaNO_3 solution containing different concentrations of phthalic acid at pH 4.0, (\square) $2.5 \text{ }\mu\text{M}$, (\bullet) $40 \text{ }\mu\text{M}$.

Figure 5. The dependence of electric charge passed after ex-situ preadsorbed for 30min in 0.1 M NaNO_3 containing different concentrations at pH 4.0 on the concentration of phthalic acid .

Figure 6. The fitting of the isotherm to Langmuir adsorption model.

Figure 7. Comparison of surface speciation distribution of TiO_2 surface groups (experimental results of Kormann et. al [28])(a), speciation distribution of phthalic acid in solution (b), the adsorption dependence of phthalic acid on pH (c).

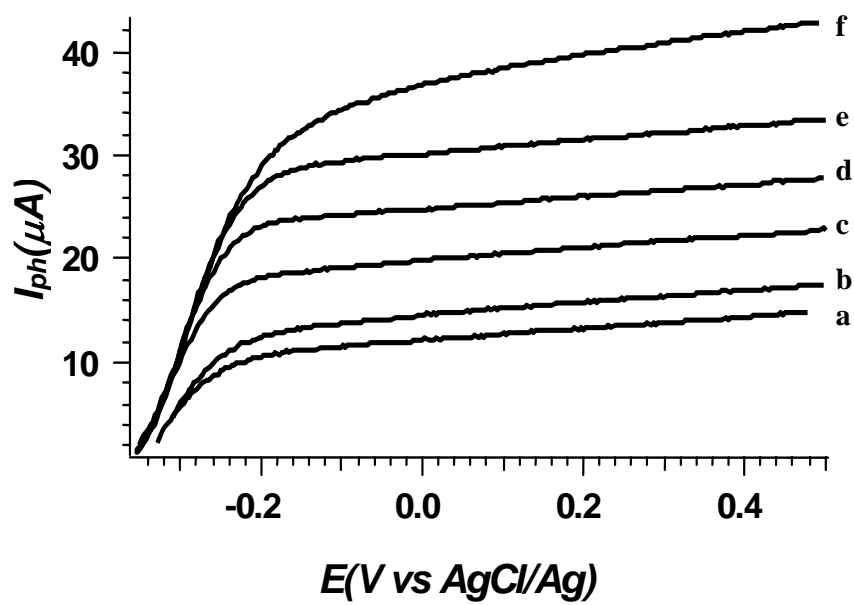


Figure 1

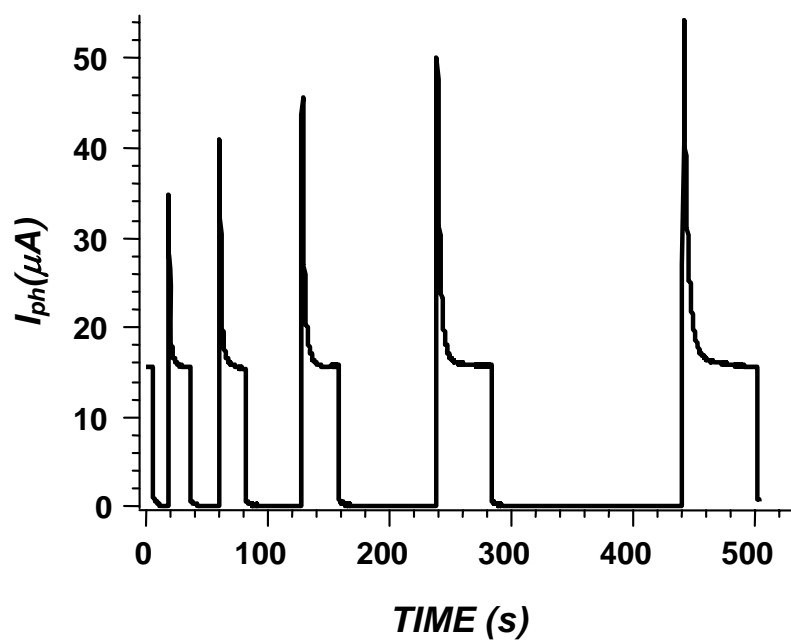


Figure 2

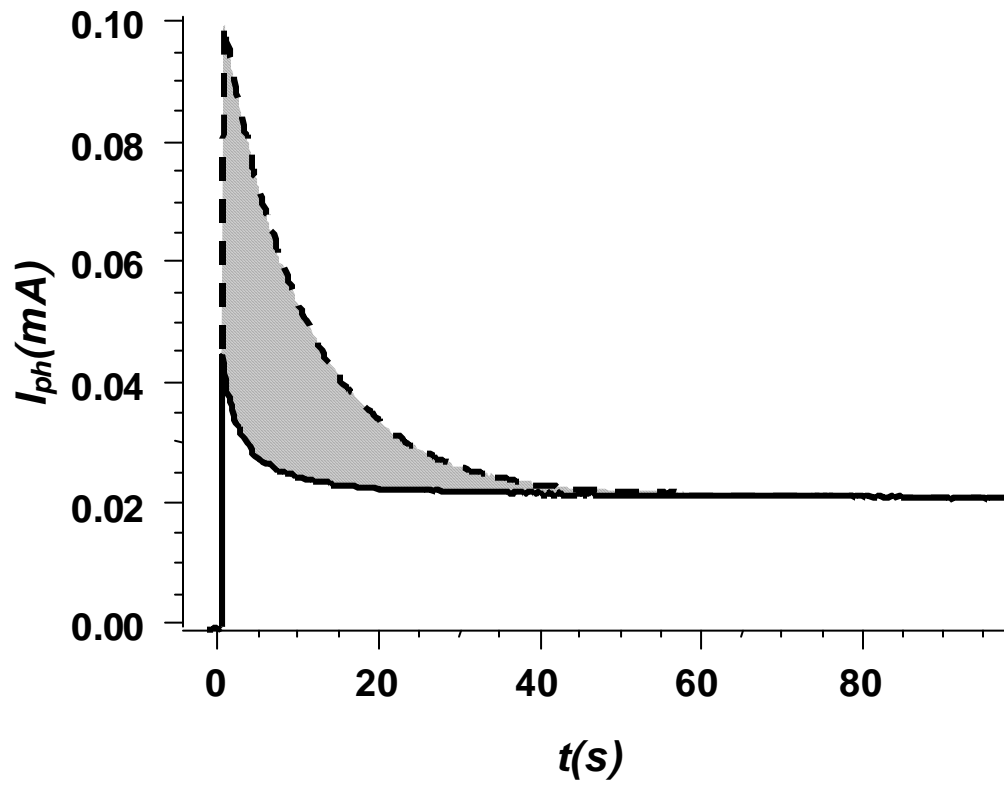


Figure 3

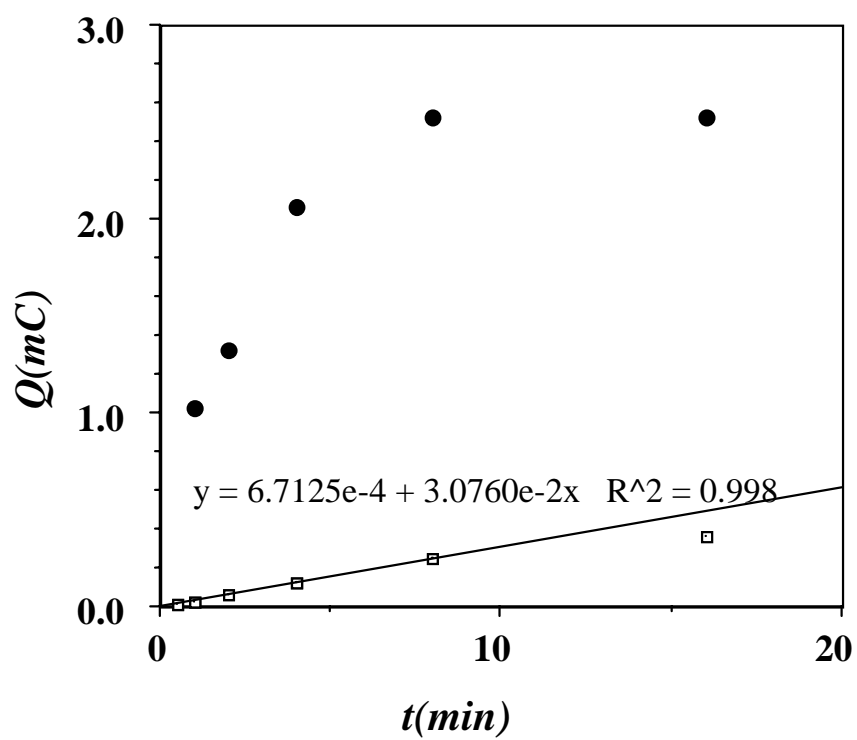


Figure 4

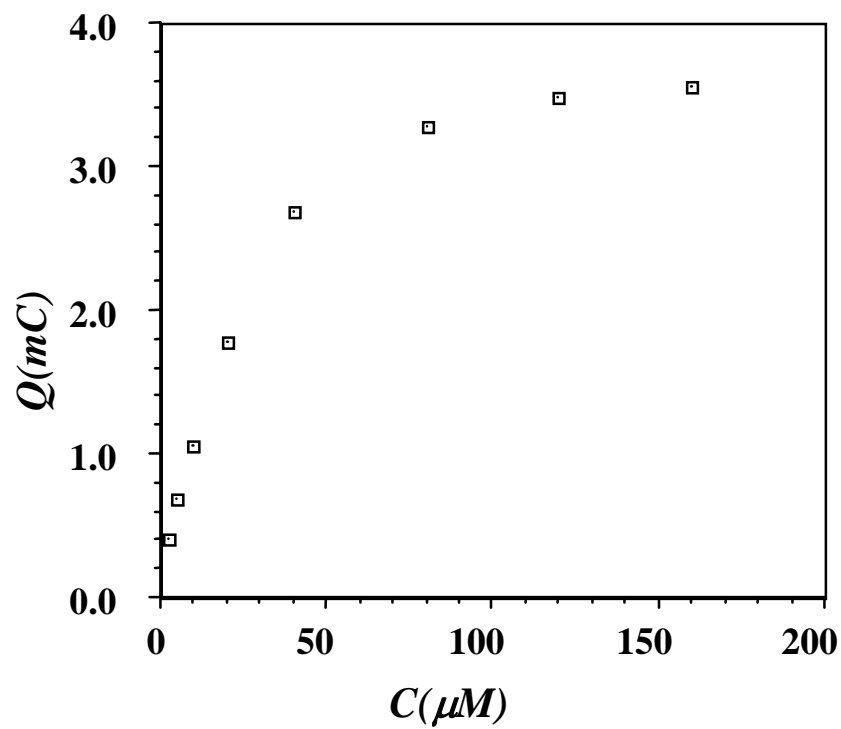


Figure 5

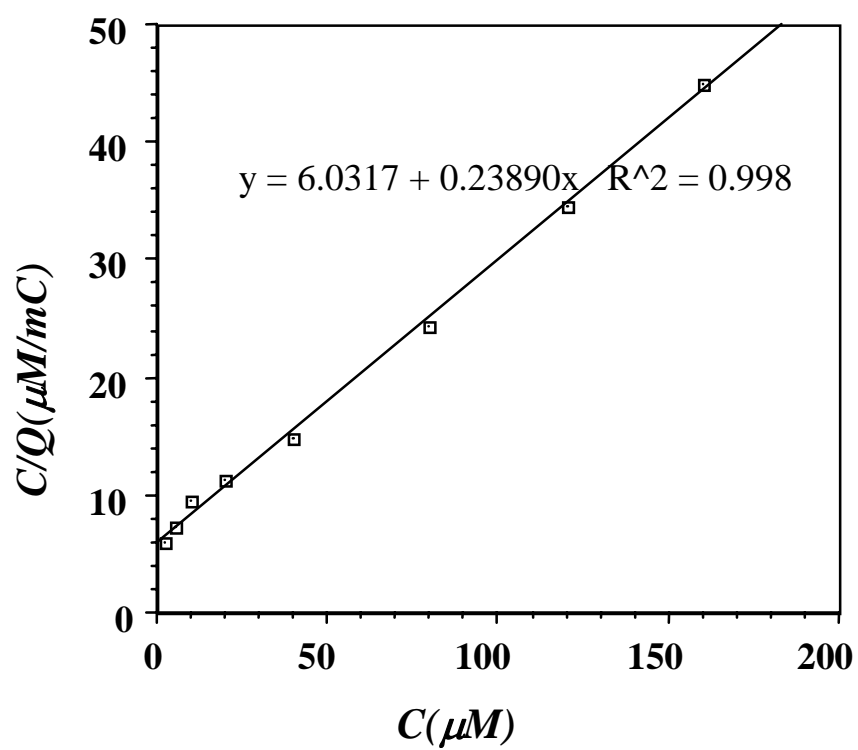


Figure 6

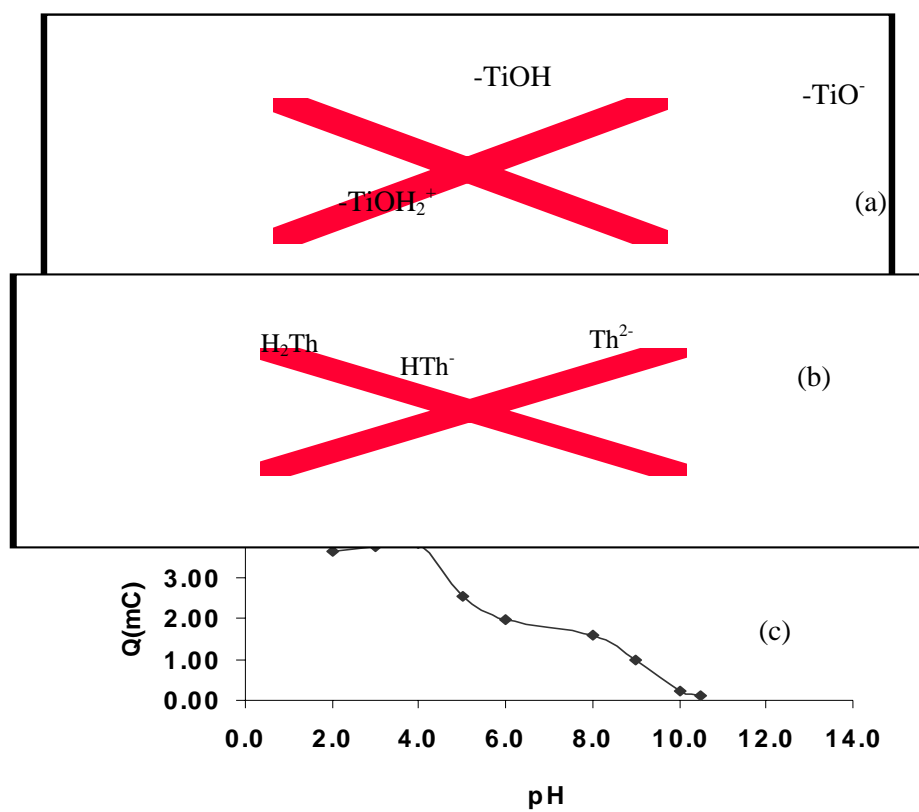


Figure 7